

Motional diminishing of optical activity: a novel method for studying molecular dynamics in liquids and plastic crystals

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Abstract

Molecular dynamics calculations and optical spectroscopy measurements of weakly active infrared modes are reported. The results are qualitatively understood in terms of the “motional diminishing” of IR lines, a process analogous to the motional narrowing of a nuclear magnetic resonance (NMR) signal. In molecular solids or liquids where the appropriate intramolecular resonances are observable, motional diminishing can be used to study the fluctuations of the intermolecular interactions having time scales of 1psec to 100psec.

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Group theory of molecular symmetries is extensively used in infrared and Raman spectroscopies to assign vibrational modes to point group representations. One of the simplest and most important arguments applies to molecules with a center of inversion symmetry: the vibrations can be divided into symmetric (*gerade*, denoted g) and asymmetric (*ungerade*, denoted u) modes; only a u mode may have IR-activity and only a g mode is allowed in the Raman spectrum. Except for the simplest molecules, further analysis is needed to determine if the modes are indeed allowed; the u modes with other than vector symmetry are IR-forbidden, and the g modes with other than tensor symmetry are Raman forbidden.

The symmetry group of an isolated molecule is strictly relevant only for low density gas phase samples. Intermolecular interactions break the pure molecular symmetry. In the gas phase, “collision induced scattering” (CIS) has been observed for some time, leading to an enhanced Rayleigh tail in noble gases [1,2], a broadening of the Raman line in SF_6 [3] and the appearance of “forbidden” IR modes in the Raman spectrum of CO_2 [4]. In liquids the intermolecular forces are even stronger and a large body of literature discusses the various manifestations of these interactions [5–9]. In the solid state the static perturbation leads to the well known crystal field splittings of degenerate modes, in addition to the appearance of previously “forbidden” resonances in the spectrum [10–14].

For disordered systems the treatment often starts in terms of two experimental time scales: the energy relaxation time T_1 and the dephasing time T_2 [7,15]. These times are analogous to T_1 and T_2 in nuclear magnetic resonance (NMR) [16]. T_1 tells us how fast the energy of a given vibration is dissipated to other modes; T_2 is the time required for the oscillators in the ensemble to develop a 2π phase difference. Since in many systems $T_1 \gg T_2$, the width of a resonance line is, in good approximation, $\Delta\omega = 1/T_2$.

The theory of the gas and the solid phases are relatively easy to handle, whereas the liquid presents a greater challenge. For CIS in the gas phase the dephasing is viewed as a result of independent collision processes, separated by the average time between collisions τ_c . Each collision adds a small random phase to the oscillations; consequently, $\Delta\omega \sim 1/\tau_c$. The magnitude of phase shift depends on the “violence” of the collision relative to the strength

of the oscillator. A detailed calculation results in $\Delta\omega = (k_B T)/(\omega^2 L^2 m \tau_c)$, where $k_B T$ is the thermal energy, L is the range of interaction and m is a mass factor [17]. In the crystalline solid state the problem is formulated in terms of the exchange coupling energy V between the oscillators: the line splittings will be of the order of $\delta\omega \propto V$. In a disordered solid the a linewidth $\Delta\omega \propto \langle V^2 \rangle^{1/2}$ is expected, where $\langle \rangle$ represents an appropriate average over all configurations.

Approaching from these two extremes, the liquid can be either viewed as a dense gas, or as a disordered, fluctuating solid. A great amount effort has been concentrated on adapting the gas phase results to liquids [17], including calculations taking into account the microscopic details of the interaction potential [9,18]. In this Communication we will take the other route. We will investigate what happens to the linewidth of the allowed resonance lines, and to the width and strength of the “forbidden” lines, if fluctuations are introduced to a quasi-static, random system. We perform computer simulations on a classical vibrational model and we use CS_2 as a model system in the experiments. The agreement we find between the measurement and the calculations should not be viewed as an exhaustive and quantitative explanation for the behavior of the spectral lines, however the results do point to a novel contributing mechanism, which we term “motional diminishing”.

Qualitatively, as the correlation time of the fluctuations (τ) decreases, one expects that the effective symmetry breaking field will disappear. This is evident in the limit of extremely fast fluctuations, when $\tau < T$ (where $T = 2\pi/\omega$, the period of oscillation of the molecular vibration in question) the external fields are expected to completely average out, producing effectively no symmetry breaking. Consequently, *i.* the linewidth of the allowed resonances narrows, $\Delta\omega \propto \tau$ [15], and *ii.* the weakly allowed lines disappear. The question is, what is the critical timescale of the fluctuations for this crossover to occur? While the first effect (“motional narrowing”) has been discussed before [7,15], the crossover from weak optical activity to no activity as the correlation time of the fluctuations decreases is a novel phenomena; we call it motional diminishing.

In addition to shedding a new light on the behavior of molecular liquids, our consid-

erations are directly applicable to “plastic” crystals [19]. In fact the main motivation of this work originated from the desire to understand the behavior of a new and particularly interesting plastic crystal, C₆₀ [20–22]. In a plastic crystal the molecules perform rotational diffusion, while preserving their center of mass positions at the crystallographic coordinates. If viewed from the reference frame of a given molecule, the *magnitude* of the crystal field does not change much but its *direction* seems to fluctuate with a correlation time τ , the rotational diffusion time constant. Note that τ and τ_c from CIS have opposite effects: $\Delta\omega \propto \tau$ and $\Delta\omega \propto 1/\tau_c$.

We performed computer simulations by solving the classical equations of motion for a simple, one dimensional, harmonic model system, in the presence of a harmonic driving field E of angular frequency ω , and fluctuating external perturbations. The time averaged power dissipation was calculated by integrating the field \times charge \times velocity at various values of the drive frequency. The “ball and spring” system is similar to a CS₂ or CO₂ molecule (except that it does not model the bending mode): it consists of two balls of equal mass m and charge q attached to a third ball of mass M and charge Q by equivalent springs of spring constant k . This “molecule” has a center of inversion symmetry with one Raman-active g mode and one IR-active u mode. The external symmetry breaking perturbation is represented by two springs, k' and k'' , connected to the two outer masses. The Hamiltonian of this system is,

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{p_3^2}{2M} + \frac{1}{2}k(x_1 - x_3)^2 + \frac{1}{2}k(x_2 - x_3)^2 \\ + E[q(x_1 + x_2) + Qx_3] + \frac{1}{2}k'x_1^2 + \frac{1}{2}k''x_2^2. \quad (1)$$

Randomness of the external perturbation is achieved by making the strengths of these outer springs fluctuate randomly. The fluctuations are characterized by a correlation time τ ; the probability of switching to a new random value of k' (or k'') in time interval dt is $dp = dt/\tau$. All other effects of the environment, the coupling to other modes, *etc.*, are represented by a damping force proportional to the velocity of the masses, with damping constant γ for all three balls. This damping provides a finite width for each resonance mode even if no outside perturbation is provided. Typical numerical values were $k = 1$, $m = M = 1$, $q = -1$,

$Q = +2$ and $\gamma = 0.005$.

If one side of the system is perturbed by an time-independent potential (represented by k'), then two resonance lines are observed: a weak one close to the “forbidden” g mode frequency $\omega = \omega_0 = \sqrt{k/m}$ and a strong one around the u mode, $\omega = \sqrt{3}\omega_0$. The line shifts from the “ideal” positions are linear in $\kappa = k'/k$; the line intensity of the “forbidden” resonance is proportional to κ^2 .

First we consider random fluctuations where a perturbing spring of fixed magnitude is randomly switched between the left and right sides, the unperturbed side having zero external coupling. In this system (referred to as “case I” later), the resonance mode frequency is the same for both the “left” and “right” perturbations, and therefore there is no additional line broadening due to the external forces. We find that slowly fluctuating perturbations produce a weak IR mode close to $\omega = \omega_0$, but this “forbidden” resonance vanishes as the correlation time τ becomes less than the lifetime of the resonance $\tau < T_1 = 1/\gamma$. Note that the line narrows even if τ is much longer than the period of the oscillation.

A more realistic model should involve random fluctuations in the magnitude of the external perturbations (this will be case II). Figures 1 and 2 summarize the results obtained when the k' and k'' spring constants were assumed to vary independently and randomly with a uniform probability distribution in the range of $0 < \kappa < \kappa_{max} = 0.4$. For quasi-static perturbations (long correlation times such as $\tau = 5000$) the u mode and the g mode resonances are both broadened beyond the lifetime effects seen in case I (the quasi-static linewidth $\Delta\omega(\tau \rightarrow \infty) = \delta$ is larger than γ), and the center frequencies are shifted from the unperturbed frequencies to somewhat higher values. At the other time extreme, fast fluctuations (like $\tau = 5$) lead to a vanishing infrared activity of the g mode (Fig. 1). The u mode narrows to the “lifetime” width γ , and its integrated intensity remains approximately unchanged (see the upper inset of Figure 2).

The parameters in this work are deliberately selected so that the three time scales in the problem ($T = 2\pi/\omega$, $T^* \equiv 1/\delta$, and $T_1 = 1/\gamma$) are well separated. For the g mode, in the dimensionless units of the calculation, $T = 1.102$, $T^* = 18$ and $T_1 = 200$; for the u mode the

values are 1.758, 40 and 200, respectively. The insets in Figures 2 and 1 clearly indicate that the crossover from the quasi-static behavior at long τ (broadened IR line and non-zero IR intensity of the Raman line) to the fast fluctuations regime (narrowed IR line and vanishing IR-activity of the Raman line) occurs at around $\tau = T^*$ for each mode. The intensity of the “forbidden” Raman line as a function of τ is well fit by the function $I = I_0/(1 + \frac{T}{\tau})$, as demonstrated by the solid line in the inset to Figure 1. In contrast to case I, the lifetime of the resonance, T_1 , does not play a particularly important role in the physically more realistic model of case II.

According to these results, the motional narrowing of the IR line is indeed very similar [7,15] to the motional narrowing of NMR resonances [16,23]. The motional diminishing of the IR-activity of the g mode is, however, an entirely new phenomenon. We found that the inverse linewidth of the quasi-static perturbed resonance determines the crossover time. In case I this linewidth is due to lifetime broadening, in case II it is determined by the magnitude of the perturbation itself. Although our discussion was conducted in terms of a classical system, experience with quantum oscillators suggests that the main features of this crossover behavior would survive a full quantum mechanical treatment. All of these phenomena can be treated in a unified way in terms of the fluctuation-dissipation theorem [23].

We choose CS₂ as a model system to test the predictions of our theory. In this material the “forbidden” Raman lines have been studied previously in detail as a function of temperature [9,18,24] and hydrostatic pressure [25–28]. The rotational diffusion of the molecules has been studied independently by NMR, and the correlation time is well known as a function of temperature [29,30].

We measured the IR transmission by using a 0.1mm thick liquid cell, enclosed by 15mil thick, singly polished, high-resistivity Si windows. The cell was filled with Fischer Scientific spectrophotometric grade CS₂ liquid, sealed with teflon washers and mounted on the cold finger of a Helitran liquid N₂ flow refrigerator. The spectra were recorded in the 125K-300K temperature range by a Bomem MB-155 FT-IR spectrometer, using the spectra of the empty

cell as backgrounds. As shown previously, the transmission method is well suited for the investigation of weakly-active modes [31].

The spectra around the ν_1 (Raman-active stretching) mode are shown in Figure 3. At frequencies extending up to 3000cm^{-1} we clearly observe several resonances corresponding to combination modes ($\nu_3 - \nu_1$, $\nu_1 + \nu_2$, $\nu_1 + 3\nu_2$, $\nu_1 + \nu_3$, $2\nu_2 + \nu_3$, $2\nu_1 + \nu_3$, and $\nu_1 + 2\nu_2 + \nu_3$). With the sample thickness used in this measurement the IR-active ν_2 and ν_3 modes appear totally saturated. Symmetry considerations [32,33] on the unperturbed, non-harmonic system predict that the combinations composed of an odd number of IR modes are IR-active. The intensity of these modes depends on the Bose factors $n_i = n(\hbar\omega_i/k_B T)$ of the contributing fundamentals (i is the mode index of the fundamental). With the sole exception of the $\nu_3 - \nu_1$ difference mode seen in Fig. 3, the intensities of the combination modes are expected to be, and found to be, approximately independent of the temperature. In Figure 4 the integrated intensity of this difference mode is shown as a function of temperature (circles), together with the expected $|n_1 - n_3|$ temperature dependence (dashed line).

The ν_1 and the $2\nu_2$ resonances are IR-forbidden by the group theory (they are in fact the two strongest Raman modes). These lines appear in the IR spectrum either due to a symmetry-breaking from the interaction between the CS_2 molecules or between CS_2 molecules and impurities in the liquid. At low temperatures both “forbidden” lines are clearly observed. The ν_1 resonance has a Fano lineshape [34]. As the temperature is increased the lines become broader and their intensities decrease, in sharp contrast to the behavior of the “allowed” modes (independent of temperature) and the “difference” mode (increasing with temperature). However, inserting the known NMR correlation times into the motional diminishing results described above gives a complete account of the temperature dependence (Fig. 4, solid line). We emphasize that, other than matching the measured and calculated intensities at one temperature, there are no fitting parameters in the calculated lines of Fig. 4.

In a similar manner we can interpret the results of a previous pressure dependence study of the Raman spectrum of CS_2 by Ikawa and Whalley [25–27]. Increasing pressure in CS_2 is

analogous to decreasing temperature: the fluctuations slow down (τ increases). The Raman observation of the IR-active ν_2 mode being sharp at high pressures, and broadening and reducing in intensity at lower pressures (motional diminishing) can therefore be explained. Similarly the Raman-active polarized spectrum of the ν_1 mode is motionally narrowed, while the depolarized ν_1 is motionally diminished at lower pressures.

To summarize, using the results of a computer simulated model, we qualitatively explained the observed diminishing of IR-inactive vibrational modes in terms of a fluxuating molecular environment. While motional diminishing is not the sole mechanism which reduces the intensity of weak spectroscopic features [8], we have shown that in appropriate situations its effect can be a significant contributor. The results discussed in this work can be utilized to measure fluctuating time scales in solids, liquids and glassy systems. In a more complex system with IR- and Raman-silent modes, *all* weakly active fundamentals may exhibit similar motional diminishing given proper symmetry breaking fluctuations. By investigating the temperature dependence of the intensity of these weak modes, molecular fluctuations falling into the timescale range determined by the experimentally resolved linewidths of spectrometers, typically 300GHz-30THz, can be studied.

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REFERENCES

- [1] H.B. Levine and G. Birnbaum, Phys. Rev. Lett. **20**, 439 (1968).
- [2] J.P. McTague and G. Birnbaum, *ibid* **21**, 661 (1968).
- [3] W. Holczer and Y.le Duff, Phys Rev. Lett. **32**, 205 (1974).
- [4] W. Holczer and R. Ouillon, Mol. Phys. **36**, 817 (1978).
- [5] J. Jonas and Y.T. Lee, J. Phys. Conens. Matter **3**, 305 (1991), and references therein.
- [6] “Phenomena Induced by Intermolecular Interactions”, Ed. G. Birnbaum (Plenum, New York, 1985) .
- [7] D.W. Oxtoby, J. Chem. Phys. **87**, 3028 (1983), and references therein.
- [8] “Collision and Interaction Induced Spectroscopy” Eds. G.C. Tabisz and M.N. Neuman (Kluwer, Dordrech, 1995).
- [9] P.A. Madden and T.I. Cox, Mol. Phys. **43**, 287 (1981).
- [10] K.D. Bier, H.J. Jodl and A. Loewenhuss, Chem. Phys. Lett. **115**, 34 (1985).
- [11] A. Anderson, *et al.*, *ibid* **21**, 9 (1973).
- [12] H. Yamada and W.B. Person, J. Chem. Phys. **40**, 309 (1964).
- [13] F. Bertinelli *et al.*, Chem. Phys. Lett. **41**, 95 (1976).
- [14] C.C. Homes, P.J. Horoyski, M.L.W. Thewalt, and B.P. Clayman, Phys. Rev. B **49**, 7052 (1994).
- [15] R.M. Lynden-Bell, Mol. Phys. **33**, 907 (1977).
- [16] C.P. Slichter, “Principles of Magnetic Resonance”, (Harper&Row, 1963).
- [17] D.W. Oxtoby, Adv. Chem. Phys. **40**, 1 (1979).
- [18] T.I. Cox and P.A. Madden, Mol. Phys. **39**, 1487 (1980).

- [19] See, for example, P.A. Winsor in “Liquid Crystals and Plastic Crystals” Ed. G.W. Gray and P.A. Winsor, vol 1, p 48 (Wiley, New York, 1974).
- [20] W.I.F. David, R.M. Ibberson, T.J.S. Dennis, J.P. Hare, and K. Prassides, *Europhys. Lett.* **18**, 219 (1992).
- [21] J.P. Lu, X.-P. Li, and R.M. Martin, *Phys. Rev. Lett.* **68**, 1551 (1992).
- [22] P.A. Heiney, J.E. Fischer, A.R. McGhie, W.J. Romanow, A.M. Denenstein, J.P. McCauley, Jr., and A.B. Smith, *Phys. Rev. Lett.* **66**, 2911 (1991).
- [23] R. Kubo, in “Fluctuation, Relaxation and Resonance in Magnetic Systems”, ed. D. Ter Haar, Oliver and Boyd, Edinburgh, p. 23, 1962.
- [24] T.I. Cox and P.A. Madden, *Chem. Phys. Lett.* **41**, 188 (1976).
- [25] S. Ikawa and E. Whalley, *J. Phys. Chem.* **94**, 7834 (1990).
- [26] S. Ikawa and E. Whalley, *J. Chem. Phys.* **86**, 1836 (1987).
- [27] S. Ikawa and E. Whalley, *J. Chem. Phys.* **85**, 2538 (1986).
- [28] S.L. Wallen, L. Nikiel, J.Yi and J. Jonas, *Chem Phys. Lett.* **229**, 82 (1994).
- [29] H.W. Spiess *et al.*, *J. Mag. Reson.* **5**, 101 (1971).
- [30] J.R. Lyerla, D.M Grant, and R.D. Bertrand, *J. Phys. Chem.* **75**, 3976 (1971).
- [31] Michael C. Martin, Xiaoqun Du, John Kwon, and Laszlo Mihaly, *Phys. Rev. B* **50**, 173 (1994).
- [32] See for example “IR: Theory and Practice of Infrared Spectroscopy”, Alpert, Keiser and Szymanski, Plenum Press, pp. 133-137, 1970.
- [33] “Introduction to the Theory of Molecular Vibrational Spectroscopies”, Weedward, Oxford Univ. Press, pp. 329-333, 1972.

[34] This lineshape is well reproduced in our model calculations if the asymmetry in restoring force k' , k'' is accompanied with an asymmetry in the damping γ' , γ'' . For a more detailed discussion, see Michael C. Martin and Laszlo Mihaly, *to be published*.

FIGURES

FIG. 1. Time averaged power absorbed as a function of frequency, ω and random fluctuation time, τ , in the frequency range near the g mode. Inset shows the integrated intensity, its fit to the given functional form, and width of the peak as a function of τ .

FIG. 2. Time averaged power absorbed as a function of frequency, ω and random fluctuation time, τ , in the frequency range near the u mode. Upper inset shows the integrated intensity and width of the peak as a function of τ . Lower inset displays how the character of the resonance changes from Lorentzian at low τ to a mix of Lorentzian and Gaussian at high τ .

FIG. 3. A portion of the IR transmission spectrum of CS_2 as a function of temperature. Labels denote the assignment of the lines, and the origin of the temperature dependencies.

FIG. 4. Temperature dependencies of the integrated intensity of the ν_1 “forbidden” mode (squares) and the $\nu_3 - \nu_1$ difference mode (circles). Results from motional diminishing theory is shown as a solid line. The dashed line represents the Bose factor temperature dependence.







